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Carbon Networks Based on Dehydrobenzoannulenes. 3. Synthesis of Graphyne Substructures[1]

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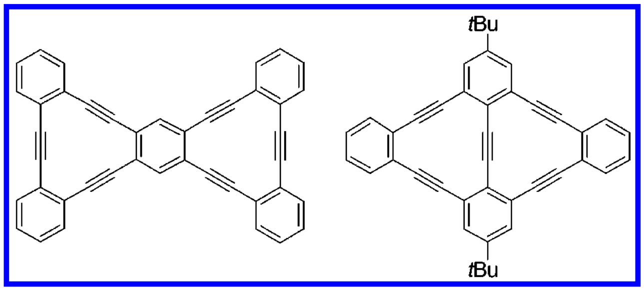
ABSTRACT



This Letter describes the synthesis of the first macrobicyclic subunits of the hypothetical all-carbon network *graphyne*. Key to synthetic success is an intramolecular Sonogashira cross-coupling sequence.

The area of highly conjugated, all-carbon and carbon-rich macromolecules continues to be of intense interest.[2] The properties of these novel systems are of great relevance in the search for organic conductors, electrochromic display materials, liquid crystals, synthetic ferromagnets, and nonlinear optical substances.[3] Recent theoretical studies predict stable, low-energy phases of carbon consisting of stacked planar carbon layers equally occupied by sp and sp^2 states.[4] Replacement of one-third of the carbon−carbon bonds of graphite with ethyne units results in the formation of one such network composed entirely of phenyl rings and triple bonds, dubbed *graphyne* (**1**). In addition to predictions of strong nonlinear optical behavior, graphyne is expected to be a large band gap semiconductor ($E_g = 1.2$ eV).[4a] Alkali metal charge-transfer complexes of **1** are predicted to be metallic.[4] Network **1** should be the most stable of the sp/sp^2 hybrid allotropes with a calculated heat of formation (ΔH_f(g,C)) of 14.2 kcal per mol of C, which is comparable to the experimentally determined values for C_{60} and C_{70} (10.16 and 9.65 kcal per mol of C, respectively).[5] Despite this thermodynamic instability, the crystalline fullerenes are kinetically stable molecules and require high temperature and pressure to force their conversion to the more stable forms of graphite and diamond; hence, graphyne might exhibit analogous kinetic stability and thus be resistant to graphitization.

Synthetic accessibility has been the primary deterrent to graphyne-related research. Controlled oligotrimerization of

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(1) For part 2 of this series, see: Wan, W. B.; Brand, S. C.; Pak, J. J.; Haley, M. M. *Chem. Eur. J.* In press.

(2) (a) *Topics in Current Chemistry (Carbon-Rich Compounds I)*; de Meijere, A., Ed.; Springer: Berlin, 1998; Vol. 196. (b) *Topics in Current Chemistry (Carbon-Rich Compounds II)*; de Meijere, A., Ed.; Springer: Berlin, 1999; Vol. 201.

(3) (a) *Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure*; Salaneck, W. R., Lundström, I., Ranby, B., Eds.; Oxford University Press: Oxford, 1993. (b) *Photonic and Optoelectronic Polymers*; Jenekhe, S. A., Wynne, K. J., Eds.; American Chemical Society: Washington, DC, 1995. (c) *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: Boca Raton, FL, 1997. (d) *Electronic Materials: The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998.

(4) (a) Baughman, R. H.; Eckhardt, H.; Kertész, M. J. *J. Chem. Phys.* **1987**, *87*, 6687−6699. (b) Narita, N.; Nagagi, S.; Suzuki, S.; Nakao, K. *Phys. Rev. B* **1998**, *58*, 11009−11014.

(5) (a) Beckhaus, H.-D.; Rückhardt, C.; Kao, M.; Diederich, F.; Foote, C. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 63−64. (b) Beckhaus, H.-D.; Verevkin, S.; Rückhardt, C.; Diederich, F.; Thilgen, C.; ter Meer, H.-U.; Mohn, H.; Müller, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 996−998.

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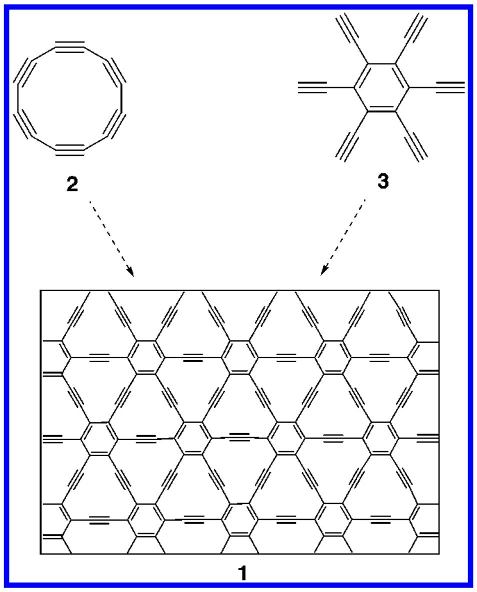
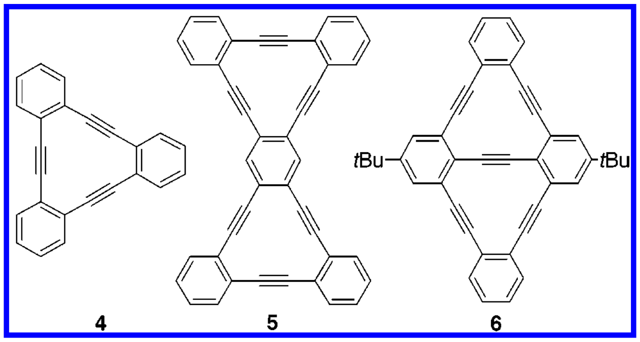
cyclo[12]carbon (**2**) could conceivably produce **1**; however, the detection of **2** outside a mass spectrometer has proven elusive.[6] Hexaethynylbenzene (**3**) can be viewed as an acetylenic scaffold off of which graphyne mimics can be built.[7] Unfortunately, **3** proved to be highly sensitive to both heat and oxygen, a common problem found in perethynylated π-systems.



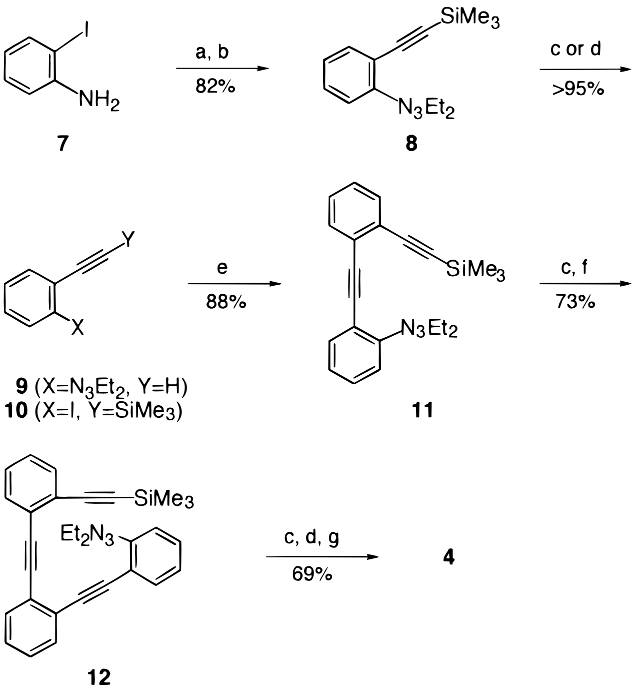
An alternative method is to prepare macrocyclic segments as network mimics. Dehydrobenzoannulenes (DBAs) are a class of molecules that are well suited for this purpose.[8] In addition to being substructures of synthetic carbon allotropes, DBAs have garnered tremendous interest in recent years as ligands for organometallic chemistry, as hosts for binding guest molecules, as probes for investigating weak induced ring currents, and as precursors to fullerenes, "bucky" tubes, "bucky" onions, and other carbon-rich materials.[9] More importantly, the annulenic compounds tend to be more stable to heat, light, and oxygen than other ethynylated π-systems. With this alternative strategy in mind, we report herein the preparation of DBAs **5** and **6**, the first macrobicyclic subunits of network **1**, and a new synthesis of **4**.[10]



Triyne **4**, the smallest subunit, has been synthesized in a variety of ways[9] over the 30+ years since its initial preparation.[11] Nevertheless, an improved version of the original approach remains the most direct route. Cu-mediated cyclotrimerization of *o*-ethynyliodobenzene provides annulene **4** in 47% yield along with an 8% yield of cyclotetramer and traces of cyclohexamer.[12] Although the cyclooligomerization strategy has furnished numerous other annulenic systems,[9] the concomitant isolation of tetramer and hexamer along with **4** suggests that use of intermolecular methods to prepare more complex structures such as **5** and/or **6** will be problematic at best.

To minimize the formation of side products, we devised an intramolecular approach for the assembly of DBAs **4**−**6**. The preparation of **4**, illustrated in Scheme 1, allowed us to test and fine-tune our synthetic route. Sequential Sonogashira cross-coupling reactions,[13] manipulation of iodines masked

Scheme 1[a]



[a] Legend: (a) i. $NaNO_2$, HCl, H_2O, ii. Et_2NH, K_2CO_3, H_2O; (b) $Me_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (c) for **9**, K_2CO_3, MeOH, THF; (d) for **10**, MeI, 120 °C; (e) **9** + **10**, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (f) **9**, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (g) $Pd(dba)_2$, PPh_3, CuI, Et_3N.

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(6) Tobe, Y.; Matsumoto, H.; Naemura, K.; Achiba, Y.; Wakabayashi, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1800−1802.

(7) Diercks, R.; Armstrong, J.; Boese, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 268−269.

(8) Haley, M. M. *Synlett* **1998**, 557−565.

(9) (a) Haley, M. M.; Pak, J. J.; Brand, S. C., in ref 2b, pp 81−130. (b) Bunz, U. H. F.; Rubin, Y.; Tobe, Y. *Chem. Soc. Rev.* **1999**, 107−119.

(10) For the synthesis of a hexaethynylated version of **4**, an "advanced" monocyclic subunit of **1**, see: Eickmeier, C.; Junga, H.; Matzger, A. J.; Scherhag, F.; Shim, M.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2103−2108.

(11) (a) Campbell, I. D.; Eglinton, G.; Henderson, W.; Raphael, R. A. *J. Chem. Soc., Chem. Commun.* **1966**, 87−89. (b) Staab, H. A.; Graf, F. *Chem. Ber.* **1970**, *103*, 1107−1118.

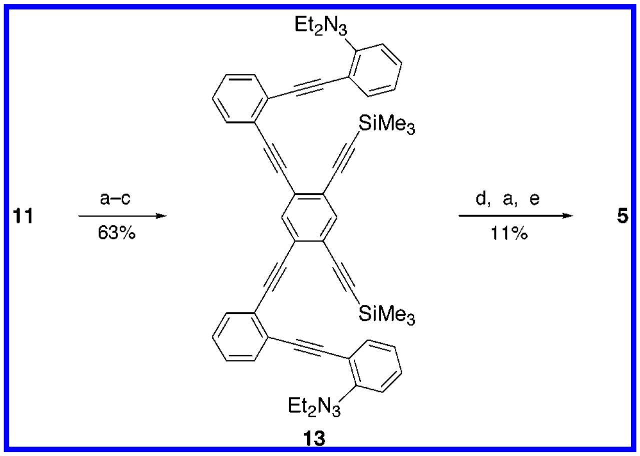
(12) Youngs, W. J.; Tessier, C. A.; Bradshaw, J. D. *Chem. Rev.* **1999**, *99*, 3153−3180 and references therein.

(13) (a) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: New York, 1995. (b) *Modern Cross-Coupling Reactions*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1997.

as dialkyltriazenes,[14] and deprotection of silylated alkynes[15] represent most of the chemistry involved in DBA construction. Diazotization of commercially available *o*-iodoaniline (**7**) and trapping with diethylamine followed by cross-coupling with (trimethylsilyl)acetylene provided triazene **8** in 82% yield. Transformation of this key intermediate into **9** or **10**[16] could be accomplished by either protiodesilylation with K_2CO_3 in MeOH or triazene decomposition with MeI at 120 °C, respectively, in essentially quantitative yield. Cross-coupling **9** with **10** afforded triazene **11**. A second iteration of triazene decomposition and cross-coupling gave triyne **12**. Triazene decomposition, protiodesilylation, and intramolecular alkynylation with $Pd(dba)_2$ under high dilution conditions furnished **4** as the sole product in 69% yield for the three steps. More importantly, larger cyclooligomeric macrocycles were not detected, facilitating product isolation and purification.

The intramolecular cyclization strategy is indispensable for the construction of more complex substructures of the graphyne network, such as bis-macrocycle **5** (Scheme 2), which are otherwise impossible to synthesize by intermolecular routes. Using the same general sequence of reactions, hexayne precursor **13** can be prepared efficiently from diyne **11**. Triazene decomposition, protiodesilylation, and 2-fold intramolecular cyclization gave, after vacuum sublimation, a yellow solid that proved to be sparingly soluble in common organic solvents. Although expected for much larger graphyne mimics, the severity of the solubility problem was surprising at this stage. It is probable that the low isolated yield of the cyclization step (<15%) is due mainly to this complication.[17]

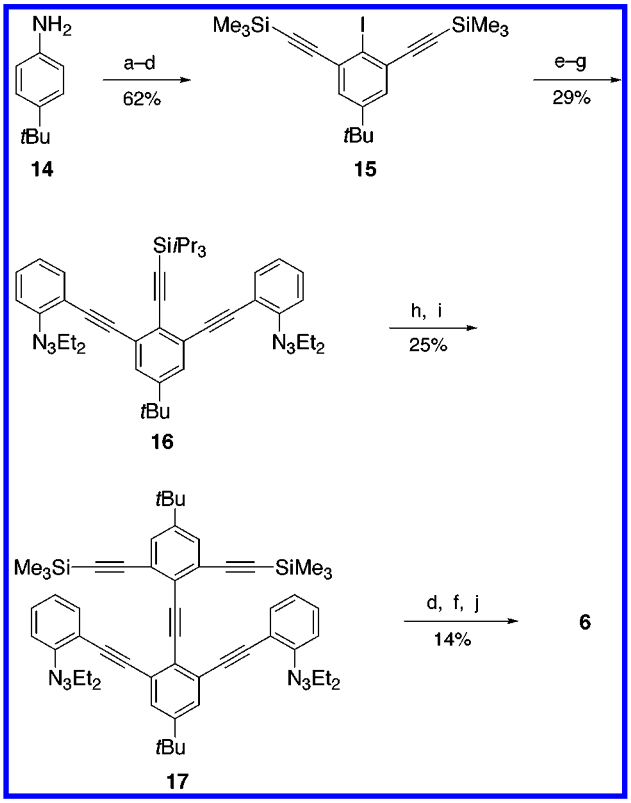
Scheme 2[a]



[a] Legend: (a) K_2CO_3, MeOH, THF; (b) 1,5-dibromo-2,4-diiodobenzene, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (c) $Me_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N, (d) MeI, 120 °C; (e) $Pd(dba)_2$, PPh_3, CuI, Et_3N.

Anticipating that solubility problems would likely be encountered during the synthesis of other graphyne subunits, solubilizing *tert*-butyl substituents were incorporated for the preparation of bis-macrocycle **6** (Scheme 3). Iodination of commercially available 4-*tert*-butylaniline with the mild reagent $(BnNEt_3)^+ICl_2^-$ [18] provided 2,6-diiodo-4-*tert*-butylaniline in high yield. This in turn was transformed into iodo intermediate **15** and subsequently triazene **16** using chemistry established in Schemes 1 and 2. Protiodesilylation and cross-coupling with a second equivalent of **15** furnished pentayne **17**. Cyclization as before gave the freely soluble, diamond-shaped subunit **6** in 0.6% overall yield for 13 steps.

Scheme 3[a]



[a] Legend: (a) $BnEt_3N^+ICl_2^-$, $CaCO_3$, CH_2Cl_2, MeOH; (b) i. $NaNO_2$, HCl, MeCN, H_2O, ii. Et_2NH, K_2CO_3, H_2O; (c) $Me_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (d) MeI, 120 °C; (e) ${}^iPr_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (f) K_2CO_3, MeOH, THF; (g) *N*,*N*-diethyl-*o*-iodophenyltriazene, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (h) $Bu_4N^+F^-$, THF, EtOH; (i) **15**, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (j) $Pd(dba)_2$, PPh_3, CuI, Et_3N.

Attempts to obtain X-ray quality crystals of the bright yellow compounds have been unsuccessful; nevertheless, the spectral properties of the molecules agree fully with the proposed structures. The IR spectra of **4**−**6** display very weak $ArC{\equiv}CAr$ stretches centered around 2200 cm^{-1}, character-

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(16) Nicolaou, K. C.; Dai, W.-M.; Hong, Y. P.; Tsay, S.-C.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 7944−7953.

(17) Repetition of the synthetic sequence with solubilizing substituents on the arenes has failed so far to furnish derivatives of **5**. Full details will be disclosed upon completion of this study.

(18) Kajigaeshi, S.; Kakinami, T.; Yamasaki, H.; Fujisaki, S.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 600−602.

istic of the highly symmetrical structures. The AA′BB′ multiplets in the ^{1}H NMR spectra of DBAs **4** and **6** are virtually superimposable ($\Delta\delta < 0.02$), with the notable exception of the four-proton singlet (δ 7.16) overlapping with the BB′ signal in **6**. Similar to that found in **4**, the upfield chemical shifts of the singlet and AA′BB′ multiplets of **6** suggest the presence of a weak paratropic ring current in the 12-membered annulenic skeleton.[19] The poor solubility of **5** precluded acquisition of meaningful NMR data.

The UV−vis spectra of **4**−**6** display the characteristic three-peak pattern of the diphenylacetylene chromophore (ca. 280, 290, and 300 nm). However, the last of these absorptions in the macrocycles is about 2.5 times more intense than the first two bands and 10 times more intense than the comparable absorption in diphenylacetylene. This strong band is attributed to the $0 \rightarrow 0$ transition of an arene $\pi-\pi^*$ excitation[11b] and is typical for the hexadehydrotribenzo[12]-annulene π-system. The UV−vis spectra of DBAs **5** and **6** do differ from that of **4** in two ways: (1) the presence of an additional moderately strong absorption around 325 nm and (2) extension of the weak, lower energy bands by an additional 50−60 nm toward longer wavelengths. This translates to end absorption points of **5** and **6** greater than 460 nm.

Typical of polycyclic aromatic hydrocarbons, the molecular ion peaks in the mass spectra of DBAs **5** and **6** (*m*/*e* 522 and 534, respectively) are also the base peaks. The mass spectra also show strong M + 1 and M + 2 peaks, reflecting the high carbon content of the bis-macrocycles. Analogous to **4**, compound **5** exhibits essentially no fragmentation; however, the presence of the two *tert*-butyl moieties in **6** results in sequential loss of the six methyl groups.

Unlike macrocycle **4**, which melts at 210 °C, DBAs **5** and **6** exhibit no melting transition prior to decomposition. DSC analyses of all three compounds show the onset of irreversible, exothermic reactions around 300−350 °C. The exotherms are extremely broad ($w^{1/2} \approx 30-40$ °C) which suggest that random polymerization of the materials is occurring. Attempts to examine the DSC thermoproducts have been severely hampered due to complete insolubility of the shiny, black materials in common organic solvents. Therefore, the structures of these thermoproducts as well as the nature of thermal transformation remain uncertain.

In summary, we have synthesized dehydrobenzoannulenes **5** and **6**, the most complete substructures of the *graphyne* all-carbon network (**1**) prepared to date, via an intramolecular cyclization strategy. In addition, we have developed an alternative preparation of subunit **4**. We are currently optimizing the syntheses in order to obtain reliable correlation studies relating macrocycle size with physical properties. These results will be the subject of a future report.

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Supporting Information Available: General experimental procedures and selected spectral data for compounds **4**−**6**, **8**−**13**, and **15**−**17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) For a discussion of induced ring currents in dehydrobenzoannulenes, see: (a) Wan, W. B.; Kimball, D. B.; Haley, M. M. *Tetrahedron Lett.* **1998**, *39*, 6795−6798. (b) Matzger, A. J.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1998**, *39*, 6791−6794.